

ful directions so kindly furnished us by Professor Stokes, and find that it shows the phenomenon in a marked manner, whether dissolved in alcohol or ether. The compound is easily decomposed by heat under ordinary circumstances, and yet can be dissolved in gaseous menstrua, and raised to a temperature of 350° without suffering any decomposition, showing the same absorption spectrum at that elevated temperature as at 15° .

We considered that it would be most interesting to examine by this method a body such as sodium, which, besides being an element, yields in the gaseous state sharp absorption lines. An opportunity seemed to be afforded by the blue solution of sodium in liquefied ammonia, described by Gore,* but we found that, on raising the ammonia above its critical point, the sodium combined with some constituent of the gas, forming a white solid, and yielding a permanent gas, probably hydrogen.

There seems, in some cases, to be a slight shifting of the absorption bands towards the red, as the temperature rises, but we have as yet been able to make no accurate measurements.

When the solid is precipitated by suddenly reducing the pressure, it is crystalline, and may be brought down as a "snow" in the gas, or on the glass as a "frost," but it is always easily redissolved by the gas on increasing the pressure. These phenomena are seen to the best advantage by a solution of potassic iodide in absolute alcohol.

We have, then, the phenomenon of a solid with no measurable gaseous pressure, dissolving in a gas, and not being affected by the passage of its menstruum through the critical point to the liquid state, showing it to be a true case of gaseous solution of a solid.

VII. "On the Action of Nuclei in producing the Sudden Solidification of Supersaturated Solutions of Glauber's Salt."

By CHARLES TOMLINSON, F.R.S. Received October 6, 1879.

I propose now to state the general conclusions at which I have arrived since resuming the study of this subject two years ago.† The remarks that will be made refer to solutions of the typical salt, sodic sulphate, in the proportions of 6 of salt to 3 of water.

In my first two papers on supersaturated saline solutions,‡ a nucleus is defined as a body that has a stronger adhesion for the salt, or for the liquid of a solution, than subsists between the salt and the liquid.

* "Proc. Roy. Soc.," vol. xxi, p. 145.

† "Proc. Roy. Soc.," vol. xxvi, p. 523.

‡ "Phil. Trans.," 1868 and 1871.

Many examples are given in which oils, fixed and volatile, alcohol, ether, &c., spreading on the surface of the solution, lead to the separation of salt, and the solidification of the solution; while, if such liquids, instead of spreading, assume a lenticular form, they become inactive, and by shaking the flask with a circular motion, are dispersed through the solution in numerous globules, without any immediate nuclear action.

There are several circumstances which favour the action of these liquid nuclei, such as (1) chemically clean flasks and solutions, so as to maintain (2) the surface-tension of the solution as high as possible, in order to spread the oils; (3) bright and clear weather, with strong evaporative force. Under such conditions the oils, &c., usually form films with nuclear action.

But it has been shown that in closed flasks, with special precautions against the entrance of particles from the air, the oils, &c., may be made to spread on the surface of these solutions without any nuclear effect.

The negative results arrived at by M. Viollette, Mr. Liversidge, and other eminent observers, led them to conclude that oils, alcohol, ether, &c., as well as porous bodies, have no action whatever on these solutions, and that the only nucleus is a salt of the same kind as the one in solution, or isomeric therewith; and that, when the oils, &c., appear to act they really contain particles of such a salt; or when the flask is uncovered for the purpose of introducing the oil, &c., such a saline speck enters from the air, which is supposed to contain saline nuclei floating about in it.

The objections made to my mode of experimenting, as well as to my conclusions, were fair enough, since, if my experiments always contained a flaw, the conclusions drawn from them would be worthless. But the thousands of results, recorded in my note books, are sufficiently harmonious to satisfy me that my mode of experimenting is trustworthy; nevertheless, I have to account for the results and conclusions of other observers which stand in direct opposition to mine.

It was a long time before I could hit upon a right method of pursuing the inquiry. At length I was led to make a number of observations daily, during some months, on the action of a freshly-distilled volatile oil on solutions of sodic sulphate, and found that during certain winds the oil was active, and that, while other winds prevailed, it was passive.*

It was clear then that, during some winds, a force was present in the air which rendered the oil active; while, during other winds, the force being absent, the oil became passive. I succeeded in identifying this force with ozone; and the point now to be determined is,

* These observations were made at Highgate. Other observations by the sea-side, &c., are noticed in "Proc. Roy. Soc.," vol. xxix, p. 24.

what is the peculiar function of ozone in rendering oils, &c., active, as nuclei?

It is evident, from the behaviour of ozone on volatile oils exposed to its influence that its action is an oxidising one, diminishing their cohesion, just as rust weakens the cohesive force of the particles in a bar of iron.

The effect which ozone produces quickly on a volatile oil is produced slowly on the same oil by long keeping. Its cohesive force is so far weakened, if not destroyed, that a drop of it on the surface of a solution no longer tends to assume the lenticular form, or to disperse in globules through the solution. Under such circumstances, since oil adheres much more strongly to salt than to water, and the super-saturated solution, being a highly charged system, capable of yielding to a force that is exerted in the right direction,* such an oil is capable of adhering to, and separating, a portion of the salt, and the action, once begun, is propagated rapidly, until the whole solution is solid.

The action of a foreign nucleus introduced into the cold solution from without, is to determine the formation of the ten-atom or normal salt: but if a solid body be boiled up with the solution, and the covered flask be left to cool to temperatures about and below 40° F., the modified or seven-watered salt will be found clustered about the solid body. An explanation of this may be found in the behaviour of the salt while undergoing solution. Suppose the flask to contain six parts of the crystallised, not effloresced, salt and three of water. If the heat be applied too strongly, the salt gives up its water of crystallisation, and the anhydrous salt is thrown down, and produces violent bumpings of the flask. But if the heat be kept below the temperature of maximum solubility of the salt (about 93° F.) until the whole of it is dissolved, the solution may be raised to the boiling point and also be cooled down in covered vessels to about 40° F., without any separation of salt. The anhydrous salt now appears to be in solution,† and a solid body previously heated in the solution forms a portion of it, or rather a portion of the flask, and may be regarded as a prolongation of its sides. Under a proper reduction of temperature, crystals of the seven-atom salt will cluster about such a body, but it cannot be said to exert any active nuclear function. It was pointed out by Ziz, as long ago as the year 1809,

* See a paper "On the Function of the sides of the Vessel in maintaining the State of Supersaturation." "Proc. Roy. Soc.," vol. xxvii, p. 189.

† See "Chemical News," 3rd and 10th December, 1869. In Wüllner's experiments on the elasticity of steam, when sodic sulphate was added to the water, the diminution in the elasticity was found to be proportional to the quantity of *dry* salt in solution at temperatures from 10° to 100° C. At the point of maximum solubility of the salt no molecular change occurred, or it would have impressed itself on the curve which represented the elasticity of the steam.

that solid bodies, boiled up with the solution, are inactive; and I have found them to be so when put into the hot or warm solution, and left till cold; and that oils and other liquids, boiled or heated with the solution, become equally inactive. Several observers, who have more or less recently worked on the subject before us, have not attended to this condition, and hence, obtaining negative results, have declared that the oils, &c., have no nuclear action under any circumstances.

If, however, a nucleus from without be introduced into the cold solution, a nucleus that is capable of adhering to the salt and not to the water of the solution, a molecule of the anhydrous salt is thereby set free, and in the very act of separating, ten atoms of water enter into combination, and thus determine the solidification of the whole of the solution in the form of the normal salt.*

If the nucleus fail to catch one of these saline molecules, as it were in the nascent state, but disperses through the solution, its effect is to lessen the adhesion between the water and the salt, and a portion of the seven-atom salt is liberated (mostly at the bottom of the vessel, where the solution is richer in salt) provided the temperature be not too high: this effect is also produced by cold alone.

If an essential oil, which acts as a nucleus in determining the formation of the normal salt, be submitted to distillation, the distillate reassumes its cohesive force, and when added to the solution, is no longer active, seeing that whether in the lenticular form, or dispersed in globules, it has a separate existence of its own, the lens and each minute globule being bound up in their own surface tension, which prevents them from coming into contact with the salt. If, however, the drop of oil spread out into a film upon the surface of the solution, the cohesion is so far weakened that adhesion between it and the salt becomes possible, separation usually takes place, and large crystals of the normal salt mould themselves on the under surface of the film.

If such be the true explanation, it is clear that any other force which diminishes or destroys the cohesive force of the oil, must confer upon it the same nuclear property. Consequently, a freshly distilled essential oil, mineral naphtha, &c., which are inactive, become active by the addition of a little absolute alcohol, ether and similar liquids in which they are soluble.

The fixed oils which tend to become rancid through age are also active, and the stearine deposited by them is especially so. Newly refined fixed oils, which are inactive, become active on the addition of a little alkali; but the tendency of potash, soda, and ammonia is to

* Löwel noticed that when the transparent seven-atom salt is removed from the solution, it becomes opaque and hot in consequence of the fixation of three additional atoms of water. In such case the supersaturated mother liquor on the surface and entangled among the crystals, produces, in the absence of a nucleus, a crystal of the normal salt by evaporation, and this acts as a nucleus.

form soluble soaps with the oils, which mingle with the solution often without nuclear action. Lime and magnesia are more manageable. On mixing the oil with one of these, and adding a drop or two to the solution, then inclining the flask nearly horizontally, and rotating it slowly on its axis, these insoluble soaps adhere to the side and form smears, upon which masses of large crystals of the normal salt start into existence in a striking manner, and the solution immediately becomes solid, so that on restoring the flask to its erect position, a vertical wall appears, with a solid mass on one side and an apparently empty space on the other.

Some of the solid and semi-solid fats in their natural state, or as they leave the hands of the cook, are admirable nuclei. Such are suet, dripping, fat of bacon and ham, lard, butter, and some others. But in all cases a freshly cut surface acts most effectually, and a fat that sometimes does not act for hours if cut one way, will act instantly if cut at right angles to the former direction. Lard contains a good deal of entangled water; this should be driven off. The lard when cold sometimes acts better when smeared on a clean glass rod than in a small lump.

The action of solid porous nuclei, such as plaster of Paris, pumice, &c., in determining the sudden solidification of these solutions admits of easy explanation. When these bodies are moderately absorptive they act by separating water from the solution; but when, by exposure to heat, their absorptive power is considerably increased, they become immediately saturated not with water, but with a portion of the solution itself, and hence there is no separation of salt. When such an apparently inactive body is exposed to the open air, its absorptive power becomes somewhat diminished by access of moisture, and it is brought into a condition to absorb more water from the solution, instead of the solution itself. In the experiments of Mr. Liversidge and others the porous bodies were thoroughly heated and dried before they were brought into contact with the solution, and this will sufficiently explain the negative results obtained by them in their carefully conducted experiments.

The action of nuclei on the supersaturated solutions of other salts that have engaged my attention, such as those of alum, zincic and magnesian sulphates, and one or two others, admits of similar explanations; but there are peculiarities belonging to each which need not at present occupy the time of the Society.

The curious condition of supersaturation was first observed by Dr. Black, towards the end of the last century, and from that time to the present innumerable notes and memoirs have been written on its varied phenomena. Some observers who have treated the subject most elaborately have adopted methods which, by the action of heat and the exclusion of air, have tended to promote the cohesive or adhesive force of

the bodies examined by them, and obtaining only negative results, and always a certain result with a crystal of the salt, they have insisted that this is the only nucleus. Others, again, have sought for an explanation in some catalytic or other mysterious force; while a third set of observers have declared it to be a matter of uncertainty or hazard whether a foreign body acts as a nucleus or not. In reviewing the subject and repeating my experiments in various ways, I see no reason for withdrawing from the theory which I had the honour of submitting to the Society eleven years ago, namely, that the action of nuclei is simply mechanical, and is capable of being expressed by the familiar word adhesion.

VIII. "On Definite Integrals involving Elliptic Functions." By J. W. L. GLAISHER, M.A., F.R.S., Fellow of Trinity College, Cambridge. Received July 31, 1879.

§ 1. The chief object of this paper is to apply to definite integrals involving elliptic functions certain special methods which have been employed for the evaluation of integrals of a similar kind involving circular functions.

§ 2. One of the most elegant and direct investigations of the value of the integral

$$\int_0^{\frac{1}{2}\pi} \log \sin x \, dx = \frac{1}{2}\pi \log \left(\frac{1}{2}\right)$$

is afforded by the product

$$\sin \frac{\pi}{n} \sin \frac{2\pi}{n} \dots \sin \frac{(n-1)\pi}{2n} = \sqrt{n} \cdot 2^{-\frac{1}{2}(n-1)},$$

for, taking the logarithm of both sides of this equation, and writing $\frac{\pi}{n} = h$,

$$\begin{aligned} h(\log \sin h + \log \sin 2h \dots + \log \sin \tfrac{1}{2}\pi) &= \pi \lim_{n=\infty} \frac{\log \{ \sqrt{n} \cdot 2^{-\frac{1}{2}(n-1)} \}}{n} \\ &= -\tfrac{1}{2}\pi \log 2. \end{aligned}$$

The same principle also gives the value of the integral

$$\int_0^{\pi} \log (1 - 2a \cos x + a^2) dx \quad \dots \quad (1),$$

which $= 0$ or $2\pi \log a$ according as $a <$ or > 1 , and it is easy to see in general that if

$$\phi\left(a + \frac{b}{n}\right) \phi\left(a + \frac{2b}{n}\right) \dots \phi\left(a + \frac{pnb}{n}\right) = \psi(n),$$

then $\int_a^{a+pb} \log \phi(x) dx = b \lim_{n=\infty} \frac{\log \psi(n)}{n} = b \frac{\psi'(\infty)}{\psi(\infty)}.$